Thermodynamics of Reactions Among Al_2O_3, CaO, SiO_2 and Fe_2O_3 During Roasting Processes

Zhongping Zhu, Tao Jiang, Guanghui Li, Yufeng Guo and Yongbin Yang
School of Minerals Processing & Bioengineering,
Central South University, Changsha, Hunan 410083,
China

1. Introduction

The thermodynamic of the chemical reactions among Al_2O_3, CaO, SiO_2 and Fe_2O_3 in the roasting processes was investigated in this chapter. The chemical reactions are classified into SiO_2-Al_2O_3 system, Fe_2O_3-Al_2O_3 system, SiO_2-Fe_2O_3 system, CaO-Al_2O_3 system, SiO_2-CaO system, SiO_2-calcium aluminates system, CaO-Fe_2O_3 system, Al_2O_3-calcium ferrites system and Al_2O_3-CaO-SiO_2-Fe_2O_3 system. When the roasting temperature is over 1100K, $3Al_2O_3 \cdot 2SiO_2$ is preferentially formed in SiO_2-Al_2O_3 system; $FeO \cdot Al_2O_3$ can be formed in Fe_2O_3-Al_2O_3 system; ferric oxide and SiO_2 could not generate iron silicate; $12CaO \cdot 7Al_2O_3$ is preferentially formed in CaO-Al_2O_3 system when one mole Al_2O_3 reacts with CaO; $2CaO \cdot SiO_2$ is preferentially formed in SiO_2-CaO system; except for $CaO \cdot 2Al_2O_3$ and $CaO \cdot Al_2O_3$, the other calcium aluminates can transform into calcium silicate by reacting with SiO_2 in SiO_2-calcium aluminates system; $2CaO \cdot Fe_2O_3$ is preferentially formed in CaO-Fe_2O_3 system; alumina is unable to form $3CaO \cdot Al_2O_3$ with calcium ferrites($2CaO \cdot Fe_2O_3$ and $CaO \cdot Fe_2O_3$), but able to form $12CaO \cdot 7Al_2O_3$ with $2CaO \cdot Fe_2O_3$; when CaO, Fe_2O_3, Al_2O_3, SiO_2 coexist, they are more likely to form ternary compound $2CaO \cdot Al_2O_3 \cdot SiO_2$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$.

2. Binary compounds

2.1 Fe_2O_3-Al_2O_3-$CaCO_3$ system

Fe_2O_3 and Al_2O_3 can all react with limestone during roasting to generate corresponding aluminates and ferrites. In Fe_2O_3-Al_2O_3-CaO system, the reaction Fe_2O_3 and Al_2O_3 with $CaCO_3$ coexist, and the reactions equations are as followed:

Reactions	A, J/mol	B, J/K.mol	Temperature, K
$CaCO_3+Al_2O_3=CaO \cdot Al_2O_3+CO_2$	161088.3	-244.1	298~1200
$CaCO_3+Fe_2O_3=CaO \cdot Fe_2O_3+CO_2$	151677.8	-220.9	298~1200

Table 1. The ΔG_T^θ of Fe_2O_3-Al_2O_3-$CaCO_3$ system （$\Delta G_T^\theta = A + BT$, J/mol; P_{CO_2} =30Pa, i.e., the partial pressure of CO_2 in the air）

The relationships between Gibbs free energy (ΔG_T^θ) and temperature (T) are as shown in figure 1.

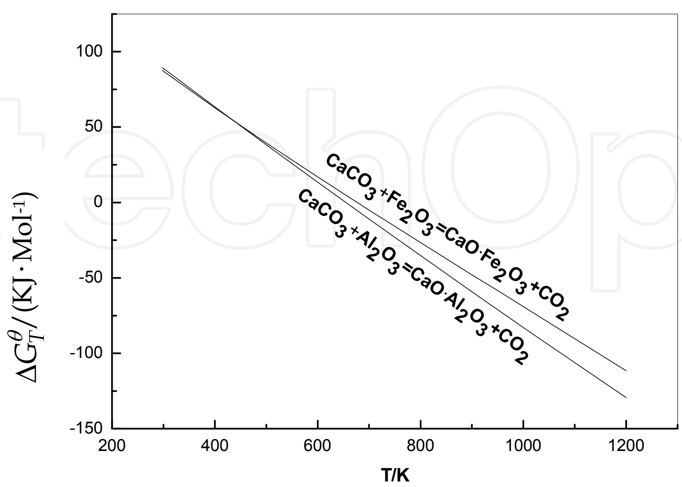


Fig. 1. Relationships between ΔG_T^θ and temperature in Fe_2O_3-Al_2O_3-$CaCO_3$ system

Figure 1 shows that, the Gibbs free energy of reactions on Fe_2O_3 and Al_2O_3 with $CaCO_3$ decreased with the rise of temperature in normal roasting process (due to decomposition of $CaCO_3$ over 1200K, so the curve has no drawing above 1200K), and the reactions all can automatically react to generate the corresponding calcium aluminate and calcium ferrite. The ΔG_T^θ of reaction with Al_2O_3 is more negative than the ΔG_T^θ of reaction with Fe_2O_3 at the same temperature. $CaCO_3$ has actually decomposed at 1473~1673K industrial roasting temperature, therefore, only CaO is taken into account on the following analysis.

2.2 SiO_2-Al_2O_3 system

SiO_2 mainly comes from the ore and coke ash in the roasting process. SiO_2 reacts with Al_2O_3 to form aluminium silicates. The aluminium silicates mainly include $Al_2O_3{\cdot}2SiO_2(AS_2)$, $Al_2O_3{\cdot}SiO_2$(AS,andalusite), AS(kyanite), AS(fibrolite), $3Al_2O_3{\cdot}2SiO_2(A_3S_2)$. Thermodynamic calculation indicates that, AS_2 can not be formed from the reaction of Al_2O_3 and SiO_2 under the roasting condition. The others equations are shown in table 2.

Reactions	A, J/mol	B, J/K.mol	Temperature, K
$Al_2O_3+SiO_2=Al_2O_3{\cdot}SiO_2$ (kyanite)	-8469.3	9.0	298~1696
$Al_2O_3+SiO_2=Al_2O_3{\cdot}SiO_2$ (fibrolite)	-4463.8	-0.9	298~1696
$Al_2O_3+SiO_2=Al_2O_3{\cdot}SiO_2$ (andalusite)	-6786.1	0.6	298~1696
$\frac{3}{2}Al_2O_3+SiO_2=(\frac{1}{2})3Al_2O_3\cdot 2SiO_2$	12764.7	-16.7	298~1696

Table 2. The ΔG_T^θ of Al_2O_3-SiO_2 system ($\Delta G_T^\theta = A + BT$, J/mol)

The relationships of ΔG_T^θ and temperature in Al_2O_3-SiO_2 system is shown in figure 2.

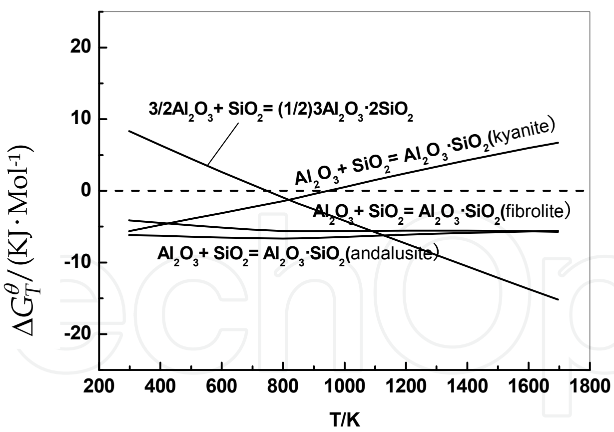


Fig. 2. Relationships of ΔG_T^θ and temperature in Al_2O_3-SiO_2 system

Figure 2 shows that, the ΔG_T^θ of kyanite is greater than zero at 1000~1700K, so the reaction cannot happen; the ΔG_T^θ of andalusite and fibrolite alter little with temperature changes; the ΔG_T^θ of A_3S_2 decreases with the rise of temperature. The thermodynamic order of forming aluminium silicates is A_3S_2, AS(andalusite), AS(fibrolite) at 1100~1700K.

2.3 Fe_2O_3-Al_2O_3 system

Al_2O_3 does not directly react with Fe_2O_3, but Al_2O_3 may react with wustite (FeO) produced during roasting process to form $FeO \cdot Al_2O_3$. No pure ferrous oxide (FeO) exists in the actual process. The ratio of oxygen atoms to iron atoms is more than one in wustite, which is generally expressed as Fe_xO(x=0.83~0.95), whose crystal structure is absence type crystallology. For convenience, FeO is expressed as wustite in this thesis. Al_2O_3 may react with wustite(FeO) to form $FeO \cdot Al_2O_3$ in the roasting process. The relationship of ΔG_T^θ and temperature is shown in figure 2, and the chemical reaction of the equation is as followed:

$$Al_2O_3+FeO=FeO \cdot Al_2O_3 \quad \Delta G_T^\theta=-30172.2+9.3T, \text{J.mol}^{-1} \quad 843\sim1650K \tag{1}$$

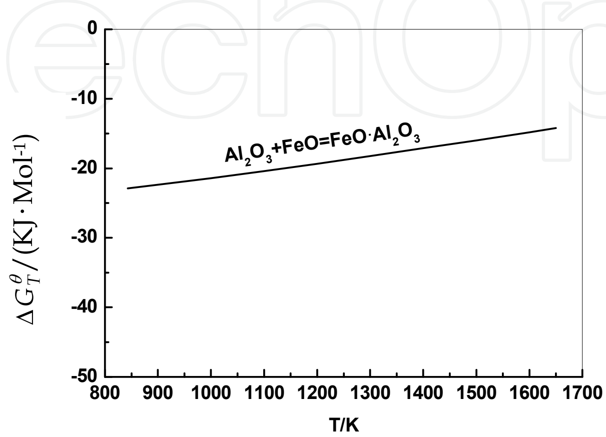


Fig. 3. Relationship of ΔG_T^θ and temperature in Fe_2O_3-Al_2O_3 system

Figure 3 shows that, the ΔG_T^θ is negative at 843~1650K, reaction can happen and generate $FeO \cdot Al_2O_3$; the ΔG_T^θ rises with the temperature, the higher temperature is, the lower thermodynamic reaction trends.

2.4 SiO_2-Fe_2O_3 system

SiO_2 also does not directly react with Fe_2O_3, but Al_2O_3 may react with wustite (FeO) to form $FeO \cdot SiO_2$ (FS) and $2FeO \cdot SiO_2$(F_2S). The relationships of ΔG_T^θ and temperature is shown in figure 4, and the chemical reactions of the equations are shown in table 3.

Reactions	A, J/mol	B, J/K.mol	Temperature, K
$FeO+SiO_2 = FeO \cdot SiO_2$	26524.6	18.8	847~1413
$2FeO+SiO_2 = 2FeO \cdot SiO_2$	-13457.3	30.3	847~1493

Table 3. The ΔG_T^θ of SiO_2- Al_2O_3 system （$\Delta G_T^\theta = A + BT$, J/mol）

Figure 4 shows that, the ΔG_T^θ of SiO_2- Al_2O_3 system are above zero at 847~1500K, so all of the reactions can not happen to form ferrous silicates (FS and F_2S).

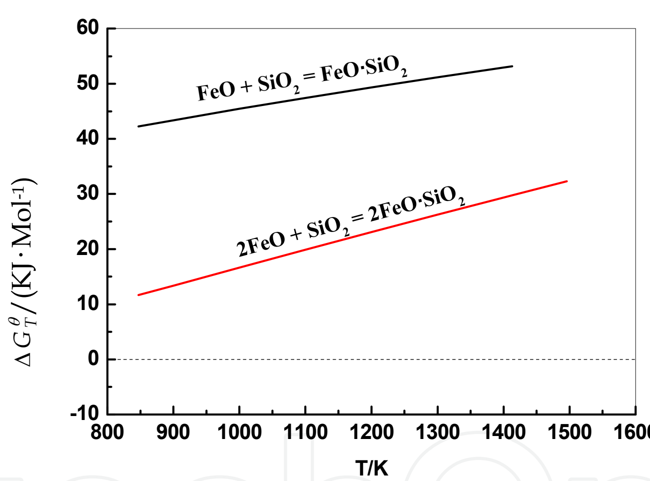


Fig. 4. Relationships of ΔG_T^θ and temperature in SiO_2-Fe_2O_3 system

2.5 CaO-Al_2O_3 system

Al_2O_3 can react with CaO to form calcium aluminates such as $3CaO \cdot Al_2O_3$(C_3A), $12CaO \cdot 7Al_2O_3$($C_{12}A_7$), $CaO \cdot Al_2O_3$(CA) and $CaO \cdot 2Al_2O_3$ (CA_2). As regard as the calcium aluminates only $C_{12}A_7$ can be totally soluble in soda solution, C_3A and CA dissolve with a slow speed, and the other calcium aluminates such as CA_2 are completely insoluble. Equations that Al_2O_3 reacted with CaO to form C_3A, $C_{12}A_7$, CA and CA_2 are presented in table 4.

Figure 5 shows that, the ΔG_T^θ of reactions of Al_2O_3 with CaO decreases with the rise of temperature; all reactions automatically proceed to generate the corresponding calcium aluminates at normal roasting temperature (1473~1673K, same as follows); At the same roasting temperature, the thermodynamic order that one mole Al_2O_3 reacts with CaO to generate calcium aluminates such as $C_{12}A_7$, C_3A, CA, CA_2.

Reactions	A, J/mol	B, J/K.mol	Temperature, K
$3CaO+Al_2O_3=3CaO\cdot Al_2O_3$	-9.9	-28.4	298~1808
$\frac{12}{7}CaO+Al_2O_3=(\frac{1}{7})12CaO\cdot 7Al_2O_3$	318.3	-44.5	298~1800
$CaO+Al_2O_3=CaO\cdot Al_2O_3$	-15871.5	-18.1	298~1878
$\frac{1}{2}CaO+Al_2O_3=(\frac{1}{2})CaO\cdot 2Al_2O_3$	-6667.2	-13.8	298~2023

Table 4. The ΔG_T^θ of Al_2O_3-CaO system（$\Delta G_T^\theta = A + BT$, J/mol）

The relationships between ΔG_T^θ and temperature (T) are shown in figure 5.

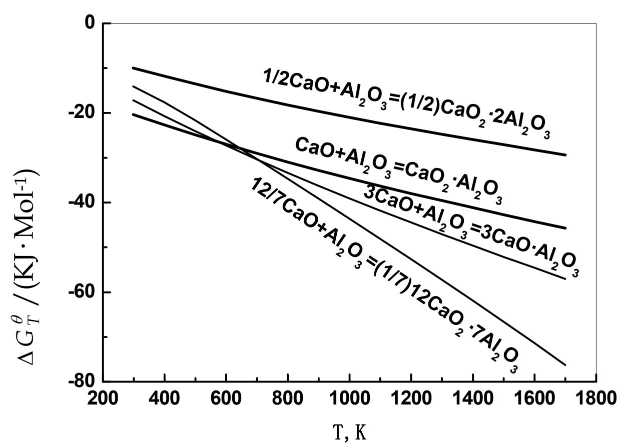


Fig. 5. Relationships between ΔG_T^θ and temperature in Al_2O_3-CaO system

Reactions	A, J/mol	B, J/K.mol	Temperature, K
$(\frac{4}{3})3CaO\cdot Al_2O_3+Al_2O_3=(\frac{1}{3})12CaO\cdot 7Al_2O_3$	13939.7	-65.8	298~1800
$(\frac{1}{2})3CaO\cdot Al_2O_3+Al_2O_3=(\frac{3}{2})CaO\cdot Al_2O_3$	-18843.8	-13.0	298~1878
$(\frac{1}{5})3CaO\cdot Al_2O_3+Al_2O_3=(\frac{3}{5})CaO\cdot 2Al_2O_3$	-6011.2	-10.9	298~2023
$(\frac{1}{5})12CaO\cdot 7Al_2O_3+Al_2O_3=(\frac{12}{5})CaO\cdot Al_2O_3$	-38544.8	18.8	298~1878
$(\frac{1}{17})12CaO\cdot 7Al_2O_3+Al_2O_3=(\frac{12}{17})CaO\cdot 2Al_2O_3$	-9541.1	-1.2	298~2023
$CaO\cdot Al_2O_3+Al_2O_3=CaO\cdot 2Al_2O_3$	2543.8	-9.5	298~2023

Table 5. The ΔG_T^θ of Al_2O_3-calcium aluminates system（$\Delta G_T^\theta = A + BT$, J/mol）

When CaO is insufficient, redundant Al_2O_3 may promote the newly generated high calcium-to-aluminum ratio (CaO to Al_2O_3 mole ratio) calcium aluminates to transform into lower calcium-to-aluminum ratio calcium aluminates. The reactions of the equations are presented in table 5:

The relationships between ΔG_T^θ of reactions of Al_2O_3-calcium aluminates system and temperature (T) are shown in figure 6.

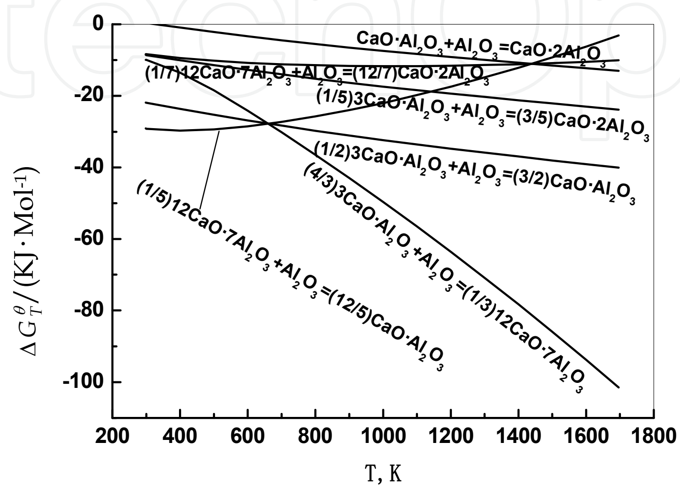


Fig. 6. Relationships between ΔG_T^θ of reactions Al_2O_3-calcium aluminates system and temperature

Figure 6 shows that, Gibbs free energy of the reaction of Al_2O_3-calcium aluminates system are negative at 400~1700K, and all the reactions automatically proceed to generate the corresponding low calcium-to-aluminum ratio calcium aluminates; Except for the reaction of Al_2O_3-$C_{12}A_7$, the ΔG_T^θ of the rest reactions decreases with the rise of temperature and becomes more negative. Comparing figure 4 with figure 5, it can be found that Al_2O_3 reacts with CaO easily to generate $C_{12}A_7$.

2.6 SiO_2- CaO system

SiO_2 can react with CaO to form $CaO\cdot SiO_2$ (CS), $3CaO\cdot 2SiO_2$ (C_3S_2), $2CaO\cdot SiO_2$ (C_2S) and $3CaO\cdot SiO_2$(C_3S) in roasting process. The reactions are shown in table 6, and the relationships between $\triangle G^0$ of the reactions of SiO_2 with CaO and temperature are shown in figure 7.

Reactions	A, J/mol	B, J/K.mol	Temperature, K
$CaO+SiO_2 = CaO\cdot SiO_2$(pseud-wollastonite)	-83453.0	-3.4	298~1817
$CaO+SiO_2 = CaO\cdot SiO_2$(wollastonite)	-89822.9	-0.3	298~1817
$\frac{3}{2}CaO+SiO_2=(\frac{1}{2})\ 3CaO\cdot 2SiO_2$	-108146.6	-3.1	298~1700
$3CaO+SiO_2 = 3CaO\cdot SiO_2$	-111011.9	-11.3	298~1800
$2CaO+SiO_2 = 2CaO\cdot SiO_2(\beta)$	-125875.1	-6.7	298~2403
$2CaO+SiO_2 = 2CaO\cdot SiO_2(\gamma)$	-137890.1	3.7	298~1100

Table 6. The ΔG_T^θ of SiO_2-CaO system($\Delta G_T^\theta = A + BT$, J/mol)

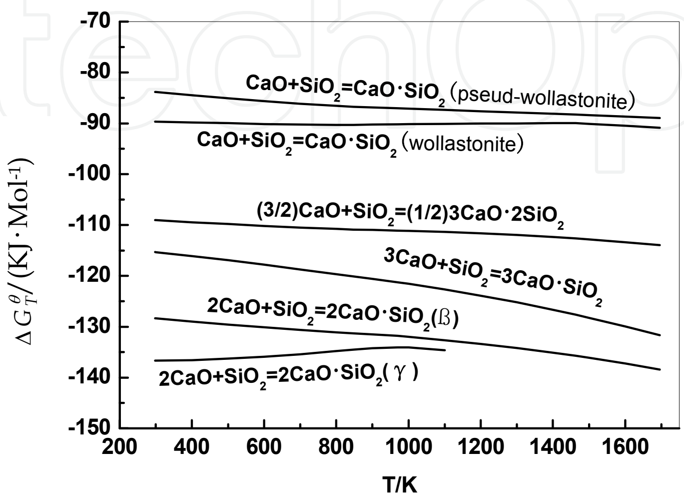


Fig. 7. Relationships between ΔG_T^θ and temperature

Figure7 shows that, SiO_2 reacts with CaO to form γ-C_2S when temperature below 1100K, but β-C_2S comes into being when the temperature above 1100K. At normal roasting temperature, the thermodynamic order of forming calcium silicate is C_2S, C_3S, C_3S_2, CS.
Figure 5 ~ figure 7 show that, CaO reacts with SiO_2 and Al_2O_3 firstly to form C_2S, and then $C_{12}A_7$. Therefore, it is less likely to form aluminium silicates in roasting process.

2.7 SiO_2- calcium aluminates system

In the CaO-Al_2O_3 system, if there exists some SiO_2, the newly formed calcium aluminates are likely to react with SiO_2 to transform to calcium silicates and Al_2O_3 because SiO_2 is more acidity than that of Al_2O_3. The reaction equations are presented in table 7, the relationships between ΔG_T^θ and temperature are shown in figure 8.

Figure 8 shows that, the ΔG_T^θ of all the reactions increases with the temperature increases; the reaction ($3CA_2+SiO_2=C_3S+6Al_2O_3$) can not happen when the roasting temperature is above 900K , i.e., the lowest calcium-to-aluminum ratio calcium aluminates cannot transform to the highest calcium-to-silicon ratio (CaO to SiO_2 molecular ratio) calcium silicate; when the temperature is above 1500K, the ΔG_T^θ of reaction($3CA+ SiO_2=C_3S+3Al_2O_3$) is also more than zero; but the other calcium aluminates all can react with SiO_2 to generate calcium silicates at 800~1700K. The thermodynamic sequence of calcium aluminates reaction with SiO_2 is firstly C_3A, and then $C_{12}A_7$, CA, CA_2.

Reactions	A, J/mol	B, J/K.mol	Temperature, K
$(3)CaO\cdot 2Al_2O_3+SiO_2=3CaO\cdot SiO_2+6Al_2O_3$	-69807.8	70.8	298~1800
$(3)CaO\cdot Al_2O_3+SiO_2=3CaO\cdot SiO_2+3Al_2O_3$	-62678.8	42.6	298~1800
$(\frac{1}{4})12CaO\cdot 7Al_2O_3+SiO_2=3CaO\cdot SiO_2+\frac{7}{4}Al_2O_3$	-111820.6	66.7	298~1800
$(2)CaO\cdot 2Al_2O_3+SiO_2=2CaO\cdot SiO_2+4Al_2O_3$	-98418.8	48.1	298~1710
$(\frac{3}{2})CaO\cdot 2Al_2O_3+SiO_2=(\frac{1}{2})3CaO\cdot 2SiO_2+3Al_2O_3$	-87585.9	38.0	298~1700
$CaO\cdot 2Al_2O_3+SiO_2=CaO\cdot SiO_2+2Al_2O_3$	-76146.6	27.1	298~1817
$CaO\cdot Al_2O_3+SiO_2=CaO\cdot SiO_2+Al_2O_3$	-73770.2	17.7	298~1817
$(\frac{3}{2})CaO\cdot Al_2O_3+SiO_2=(\frac{1}{2})3CaO\cdot 2SiO_2+\frac{3}{2}Al_2O_3$	-84021.4	23.8	298~1700
$(2)CaO\cdot Al_2O_3+SiO_2=2CaO\cdot SiO_2+2Al_2O_3$	-93666.1	29.2	298~1710
$(\frac{1}{12})12CaO\cdot 7Al_2O_3+SiO_2=CaO\cdot SiO_2+\frac{7}{12}Al_2O_3$	-90150.8	25.7	298~1800
$(\frac{1}{8})12CaO\cdot 7Al_2O_3+SiO_2=(\frac{1}{2})3CaO\cdot 2SiO_2+\frac{7}{8}Al_2O_3$	-108592.3	35.9	298~1700
$(\frac{1}{6})12CaO\cdot 7Al_2O_3+SiO_2=2CaO\cdot SiO_2+\frac{7}{6}Al_2O_3$	-126427.4	45.3	298~1710
$(\frac{1}{3})3CaO\cdot Al_2O_3+SiO_2=CaO\cdot SiO_2+\frac{1}{3}Al_2O_3$	-86654.2	9.4	298~1808
$3CaO\cdot Al_2O_3+SiO_2=3CaO\cdot SiO_2+Al_2O_3$	-100774.6	16.9	298~1808
$(\frac{1}{2})3CaO\cdot Al_2O_3+SiO_2=(\frac{1}{2})3CaO\cdot 2SiO_2+\frac{1}{2}Al_2O_3$	-103069.3	11.0	298~1700
$(\frac{2}{3})3CaO\cdot Al_2O_3+SiO_2=2CaO\cdot SiO_2+\frac{2}{3}Al_2O_3$	-119063.3	12.1	298~1710

Table 7. The ΔG_T^{θ} of the reactions SiO_2 with calcium aluminates($\Delta G_T^{\theta}=A+BT$, J/mol)

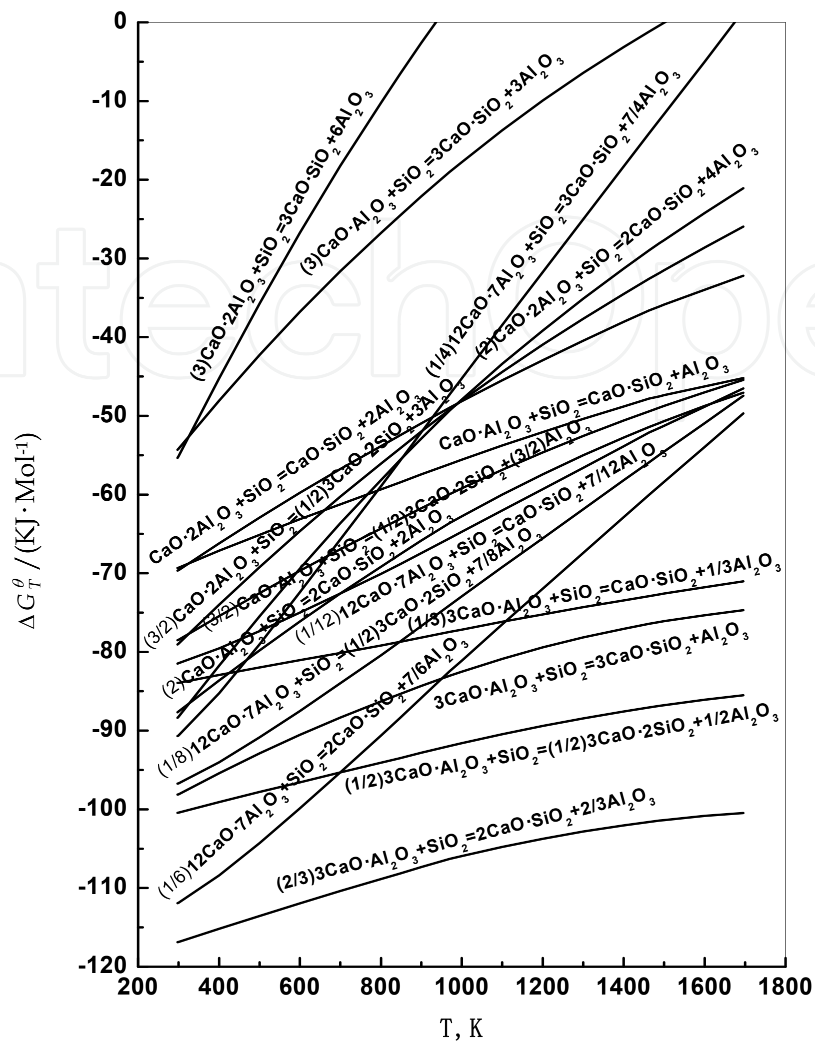


Fig. 8. Relationships between ΔG_T^{θ} and temperature in SiO_2-calcium aluminates system

2.8 CaO- Fe_2O_3 system

Fe_2O_3 can react with CaO to form CaO $\cdot Fe_2O_3$(CF) and 2CaO $\cdot Fe_2O_3$(C_2F). When Fe_2O_3 is used up, the newly formed C_2F can react with Fe_2O_3 to form CF. The reaction equations are shown in table 8, and the relationships between $\triangle G^0$ and temperature are shown in figure 9.

Figure 9 shows that, Fe_2O_3 reacts with CaO much easily to form C_2F; CF is not from the reaction of C_2F and Fe_2O_3, but from the directly reaction of Fe_2O_3 with CaO. When Fe_2O_3 is excess, C_2F can react with Fe_2O_3 to form CF.

Reactions	A, J/mol	B, J/K.mol	Temperature, K
$CaO+Fe_2O_3=CaO \cdot Fe_2O_3$	-19179.9	-11.1	298~1489
$2CaO+Fe_2O_3=2CaO \cdot Fe_2O_3$	-40866.7	-9.3	298~1723
$2CaO \cdot Fe_2O_3+Fe_2O_3=(2)CaO \cdot Fe_2O_3$	2340.8	-12.6	298~1489

Table 8. The ΔG_T^{θ} of Fe_2O_3-CaO system($\Delta G_T^{\theta} = A + BT$, J/mol)

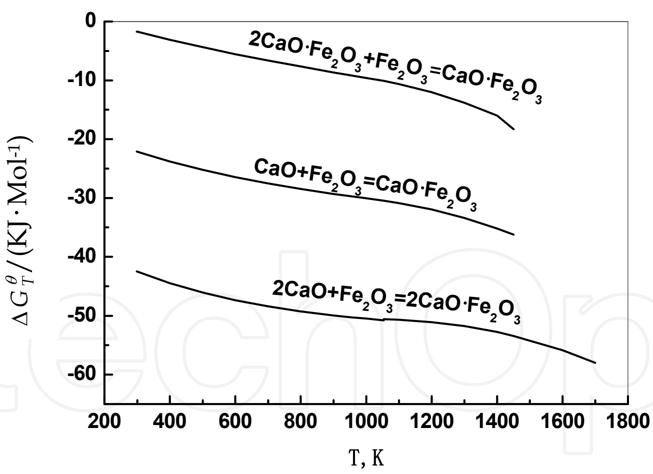


Fig. 9. Relationships between ΔG_T^θ and temperature in Fe_2O_3-CaO system

2.9 Al_2O_3- calcium ferrites system

Figure 1 shows that, the ΔG_T^θ of the reaction of Al_2O_3 with $CaCO_3$ is more negative than that of Fe_2O_3 with $CaCO_3$, therefore, the reaction of Fe_2O_3 with $CaCO_3$ occurs after the reaction of Al_2O_3 with $CaCO_3$ under the conditions of excess $CaCO_3$. The new generated calcium ferrites are likely to transform into calcium aluminates when $CaCO_3$ is insufficient, the reactions are as followed:

Reactions	A, J/mol	B, J/K.mol	Temperature, K
$(3)CaO \bullet Fe_2O_3+ Al_2O_3 = 3CaO \bullet Al_2O_3+3Fe_2O_3$	47922.7	4.5	298~1489
$(\frac{3}{2})2CaO \cdot Fe_2O_3 + Al_2O_3 = 3CaO \cdot Al_2O_3 + \frac{3}{2}Fe_2O_3$	49.6	-1.2×10^{-2}	298~1723
$(\frac{12}{7})CaO \cdot Fe_2O_3 + Al_2O_3 = (\frac{1}{7})12CaO \cdot 7Al_2O_3 + \frac{12}{7}Fe_2O_3$	32685.1	-24.5	298~1489
$(\frac{6}{7})2CaO \cdot Fe_2O_3 + Al_2O_3 = (\frac{1}{7})12CaO \cdot 7Al_2O_3 + \frac{6}{7}Fe_2O_3$	34514.4	-35.0	298~1723
$CaO \bullet Fe_2O_3+ Al_2O_3 =CaO \bullet Al_2O_3+Fe_2O_3$	3626.6	-7.5	298~1489
$(\frac{1}{2})CaO \cdot Fe_2O_3 + Al_2O_3 = (\frac{1}{2})\ CaO \cdot 2Al_2O_3 + \frac{1}{2}Fe_2O_3$	3215.1	-8.8	298~1489
$(\frac{1}{4})2CaO \cdot Fe_2O_3 + Al_2O_3 = (\frac{1}{2})\ CaO \cdot 2Al_2O_3 + \frac{1}{4}Fe_2O_3$	3168.6	-11.0	298~1723
$(\frac{1}{2})2CaO \cdot Fe_2O_3 + Al_2O_3 = CaO \cdot Al_2O_3 + \frac{1}{2}Fe_2O_3$	4009.5	-12.8	298~1723

Table 9. The ΔG_T^θ of the reaction Al_2O_3 with calcium ferrites($\Delta G_T^\theta = A + BT$, J/mol)

The relationships between ΔG_T^θ and temperature (T) are shown in figure 10. Figure 10 shows that, Al_2O_3 cannot replace the Fe_2O_3 in calcium ferrites to generate C_3A, and also cannot replace the Fe_2O_3 in $CaO \bullet Fe_2O_3$(CF) to generate $C_{12}A_7$, but it can replace the Fe_2O_3 in $2CaO \bullet Fe_2O_3$(C_2F) to generate $C_{12}A_7$ when the temperature is above 1000K, the higher temperature is, the more negative Gibbs free energy is; Al_2O_3 can react with CF and C_2F to form CA or CA_2, the higher temperature, more negative ΔG_T^θ. Because Fe_2O_3 reacts with CaO more easily to generate C_2F (Fig.9), therefore, $C_{12}A_7$ is the reaction product at normal roasting temperature(1073~1673K) under the conditions that CaO is sufficent in batching and the ternary compounds are not considered.

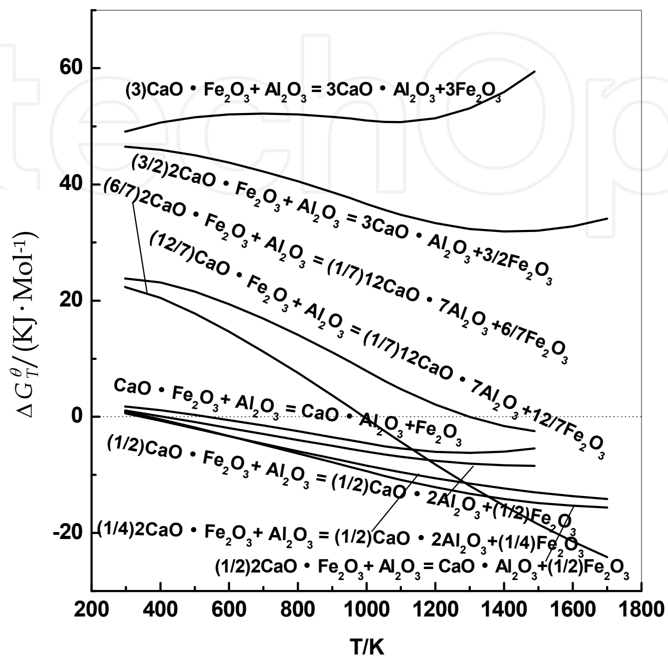


Fig. 10. Relationship between ΔG_T^θ and temperature in Al_2O_3- calcium ferrites system

3. Ternary compounds in Al_2O_3-CaO-SiO_2-Fe_2O_3 system

The ternary compounds formed by CaO, Al_2O_3 and SiO_2 in roasting process are mainly $2CaO\cdot Al_2O_3\cdot SiO_2$($C_2AS$), $CaO\cdot Al_2O_3\cdot 2SiO_2$($CAS_2$), $CaO\cdot Al_2O_3\cdot SiO_2$(CAS) and $3CaO\cdot Al_2O_3\cdot 3SiO_2$($C_3AS_3$). In addition, ternary compound $4CaO\cdot Al_2O_3\cdot Fe_2O_3$($C_4AF$) is formed form CaO, Al_2O_3 and Fe_2O_3. The equations are shown in table 10:

Reactions	A, J/mol	B, J/K.mol	Temperature, K
$CaO\cdot SiO_2 + CaO\cdot Al_2O_3 = 2CaO\cdot Al_2O_3\cdot SiO_2$	-30809.41	0.60	298~1600
$\frac{1}{2}Al_2O_3 + \frac{1}{2}CaO + SiO_2 = (\frac{1}{2})CaO\cdot Al_2O_3\cdot 2SiO_2$	-47997.55	-7.34	298~1826
$Al_2O_3 + 2CaO + SiO_2 = 2CaO\cdot Al_2O_3\cdot SiO_2$	-50305.83	-9.33	298~1600
$Al_2O_3 + CaO + SiO_2 = CaO\cdot Al_2O_3\cdot SiO_2$	-72975.54	-9.49	298~1700
$\frac{1}{3}Al_2O_3 + CaO + SiO_2 = (\frac{1}{3})3CaO\cdot Al_2O_3\cdot 3SiO_2$	-112354.51	20.86	298~1700
$4CaO + Al_2O_3 + Fe_2O_3 = 4CaO\cdot Al_2O_3\cdot Fe_2O_3$	-66826.92	-62.5	298~2000
$Al_2O_3 + 2CaO + SiO_2 = 2CaO\cdot Al_2O_3\cdot SiO_2$ (cacoclasite)	-136733.59	-17.59	298~1863

Table 10. The ΔG_T^θ of forming ternary compounds ($\Delta G_T^\theta = A + BT$, J/mol)

The relationships between ΔG_T^θ and temperature (T) are shown in figure 11. Figure 11 shows that, except for C_3AS_3(Hessonite), all the ΔG_T^θ of the reactions get more negative with the temperature increasing; the thermodynamic order of generating ternary compounds at sintering temperature of 1473K is: C_2AS(cacoclasite) , C_4AF, CAS, C_3AS_3, C_2AS, CAS_2.

C_2AS may also be formed by the reaction of CA and CS, the curve is presented in figure 11. Figure 11 shows that, the ΔG_T^θ of reaction (Al_2O_3+CaO+SiO_2) is lower than that of reaction of CA and CS to generate C_2AS. So C_2AS does not form from the binary compounds CA and CS, but from the direct combination among Al_2O_3, CaO, SiO_2. Qiusheng Zhou thinks that, C_4AF is not formed by mutual reaction of calcium ferrites and sodium aluminates, but from the direct reaction of CaO, Al_2O_3 and Fe_2O_3. Thermodynamic analysis of figure 1~figure11 shows that, reactions of Al_2O_3, Fe_2O_3, SiO_2 and CaO are much easier to form C_2AS and C_4AF, as shown in figure 12.

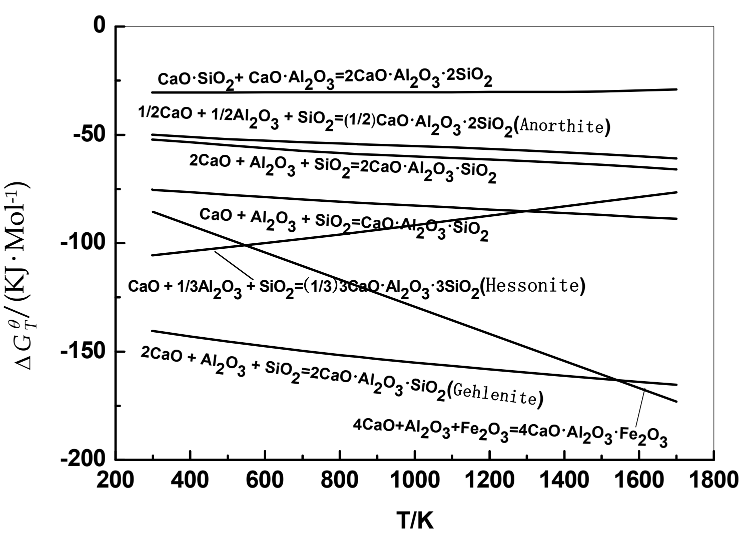


Fig. 11. Relationships between ΔG_T^θ of ternary compounds and temperature

Figure 12 shows that, in thermodynamics, C_2AS and C_4AF are firstly formed when Al_2O_3, Fe_2O_3, SiO_2 and CaO coexist, and then calcium silicates, calcium aluminates and calcium ferrites are generated.

4. Summary

1) When Al_2O_3 and Fe_2O_3 simultaneously react with CaO, calcium silicates are firstly formed, and then calcium ferrites. In thermodynamics, when one mole Al_2O_3 reacts with CaO, the sequence of generating calcium aluminates are $12CaO{\cdot}7Al_2O_3$, $3CaO{\cdot}Al_2O_3$, $CaO{\cdot}Al_2O_3$, $CaO{\cdot}2Al_2O_3$. When CaO is insufficient, redundant Al_2O_3 may promote the newly generated high calcium-to-aluminum ratio calcium aluminates to transform to lower calcium-to-aluminum ratio calcium aluminates. Fe_2O_3 reacts with CaO easily to form$2CaO{\cdot}Fe_2O_3$, and $CaO{\cdot}Fe_2O_3$ is not from the reaction of $2CaO{\cdot}Fe_2O_3$ and Fe_2O_3 but form the directly combination of Fe_2O_3 with CaO. Al_2O_3 cannot replace the Fe_2O_3 in calcium ferrites to generate $3CaO{\cdot}Al_2O_3$, and also cannot replace the Fe_2O_3 in $CaO{\bullet}Fe_2O_3$ to generate $12CaO{\cdot}7Al_2O_3$, but can replace the Fe_2O_3 in $2CaO{\bullet}Fe_2O_3$ to generate $12CaO{\cdot}7Al_2O_3$ when the temperature is above 1000K; Al_2O_3 can react with calcium ferrites to form $CaO{\cdot}Al_2O_3$ or $CaO{\cdot}2Al_2O_3$.

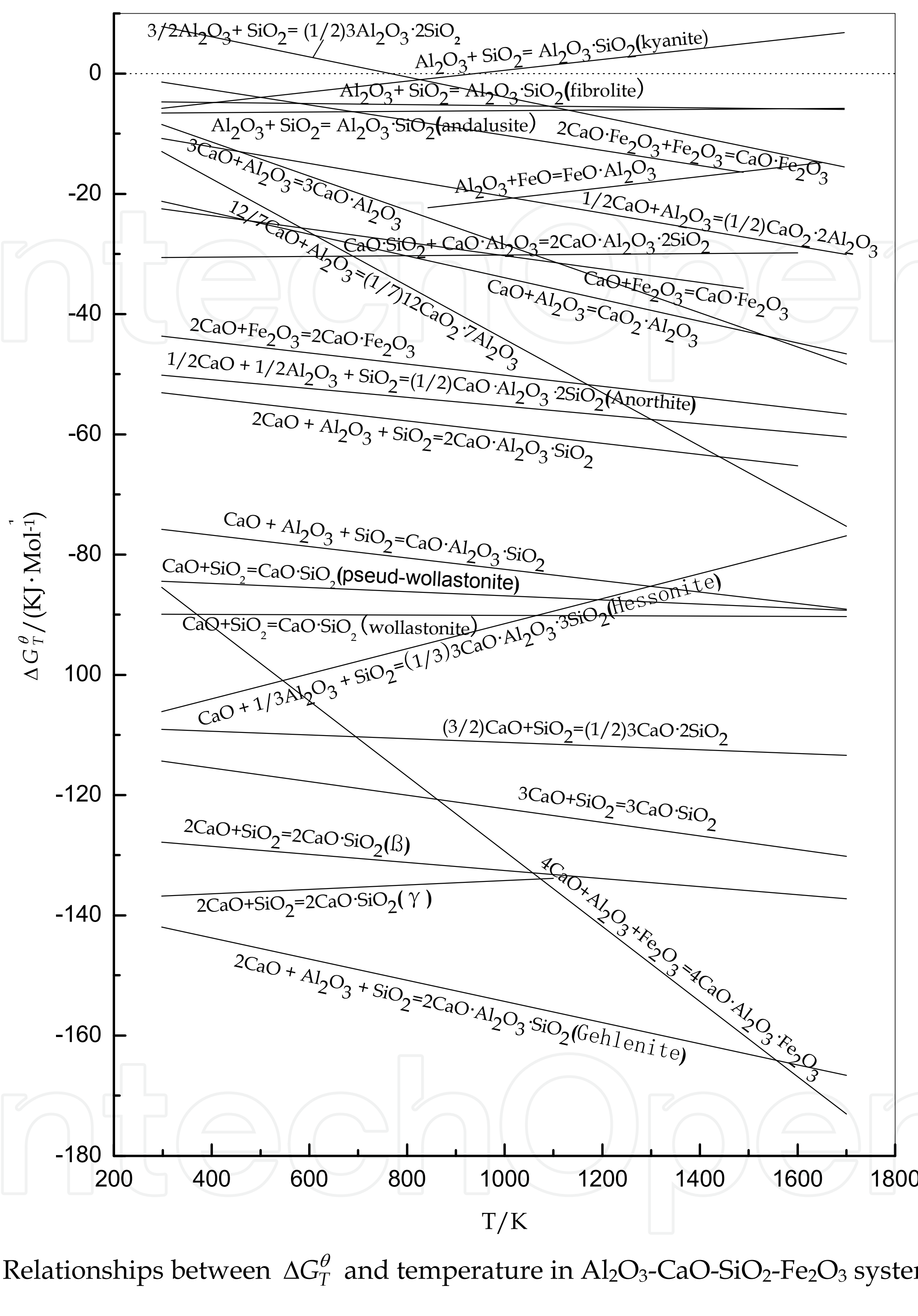


Fig. 12. Relationships between ΔG_T^{θ} and temperature in Al_2O_3-CaO-SiO_2-Fe_2O_3 system

2) One mole SiO_2 reacts with Al_2O_3 much easily to generate $3Al_2O_3{\cdot}2SiO_2$, Fe_2O_3 can not react with SiO_2 in the roasting process in the air. Al_2O_3 can not directly react with Fe_2O_3, but can react with wustite (FeO) to form $FeO{\cdot}Al_2O_3$.

3) In thermodynamics, the sequence of one mole SiO_2 reacts with CaO to form calcium silicates is $2CaO{\cdot}SiO_2$, $3CaO{\cdot}SiO_2$, $3CaO{\cdot}2SiO_2$ and $CaO{\cdot}SiO_2$. Calcium aluminates can react with SiO_2 to transform to calcium silicates and Al_2O_3. $CaO{\cdot}2Al_2O_3$ can not transform to $3CaO{\cdot}SiO_2$ when the roasting temperature is above 900K; when the temperature is above

1500K, $3CaO \cdot Al_2O_3$ can not transform to $3CaO \cdot SiO_2$; but the other calcium aluminates all can all react with SiO_2 to generate calcium silicates at 800~1700K.
4) Reactions among Al_2O_3, Fe_2O_3, SiO_2 and CaO easily form $2CaO \cdot Al_2O_3 \cdot SiO_2$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. $2CaO \cdot Al_2O_3 \cdot SiO_2$ does not form from the reaction of $CaO \cdot Al_2O_3$ and $CaO \cdot SiO_2$, but from the direct reaction among Al_2O_3, CaO, SiO_2. And $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ is also not formed via mutual reaction of calcium ferrites and sodium aluminates, but from the direct reaction of CaO, Al_2O_3 and Fe_2O_3. In thermodynamics, when Al_2O_3, Fe_2O_3, SiO_2 and CaO coexist, $2CaO \cdot Al_2O_3 \cdot SiO_2$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ are firstly formed, and then calcium silicates, calcium aluminates and calcium ferrites.

5. Symbols used

Thermodynamic temperature: T, K
Thermal unit: J
Amount of substance: mole
Standard Gibbs free energy: ΔG_T^θ ,J

6. References

Li, B.; Xu, Y. & Choi, J. (1996). Applying Machine Learning Techniques, *Proceedings of ASME 2010 4th International Conference on Energy Sustainability*, pp.14-17, ISBN 842-6508-23-3, Phoenix, Arizona, USA, May 17-22, 2010

Rayi H. S. ; Kundu N.(1986). Thermal analysis studies on the initial stages of iron oxide reduction, *Thermochimi, Acta.* 101:107~118,1986

Coats A.W. ; Redferm J.P.(1964). Kinetic parameters from thermogravimetric data, *Nature*, 201:68,1964

LIU Gui-hua, LI Xiao-bin, PENG Zhi-hong, ZHOU Qiu-sheng(2003). Behavior of calcium silicate in leaching process. *Trans Nonferrous Met Soc China*, January 213−216,2003

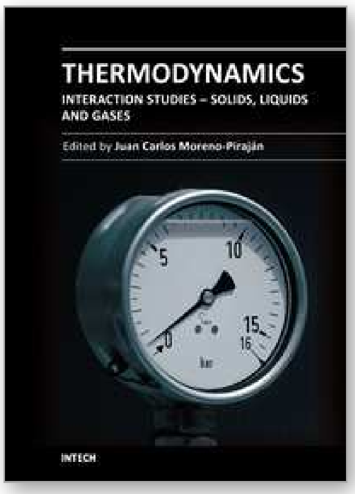
Paul S. ; Mukherjee S.(1992). Nonisothermal and isothermal reduction kinetics of iron ore agglomerates, *Ironmaking and steelmaking*, March 190~193, 1992

ZHU Zhongping, JIANG Tao, LI Guanghui, HUANG Zhucheng(2009). Thermodynamics of reaction of alumina during sintering process of high-iron gibbsite-type bauxite, *The Chinese Journal of Nonferrous Metals*, Dec 2243~2250, 2009

ZHOU Qiusheng, QI Tiangui, PENG Zhihong, LIU Guihua, LI Xiaobin(2007). Thermodynamics of reaction behavior of ferric oxide during sinter-preparing process, *The Chinese Journal of Nonferrous Metals*, Jun 974~978, 2007

Barin I., Knacke O.(1997). *Thermochemical properties of inorganic substances*, Berlin:Supplement, 1997

Barin I., Knacke O.(1973). *Thermochemical properties of inorganic substances*, Berlin: Springer, 1973



Thermodynamics - Interaction Studies - Solids, Liquids and Gases
Edited by Dr. Juan Carlos Moreno PirajÃ¡n

ISBN 978-953-307-563-1
Hard cover, 918 pages
Publisher InTech
Published online 02, November, 2011
Published in print edition November, 2011

Thermodynamics is one of the most exciting branches of physical chemistry which has greatly contributed to the modern science. Being concentrated on a wide range of applications of thermodynamics, this book gathers a series of contributions by the finest scientists in the world, gathered in an orderly manner. It can be used in post-graduate courses for students and as a reference book, as it is written in a language pleasing to the reader. It can also serve as a reference material for researchers to whom the thermodynamics is one of the area of interest.